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(54) **Preparation of zeolites**

(57) Crystalline aluminosilicate zeolites having an $SiO_2Al_2O_3$ molar ratio of at least 12 and a constraint index between 1 and 12 are prepared from an aqueous mixture containing a compound of an alkali or alkaline-earth metal (M), an Al-compound, a Si-compound, an alcohol (ROH) and ammonia. The compounds are present in the following molar ratios:
$SiO_2:Al_2O_3 \geqslant 12$; $(M)_{2/n}O:SiO_2 = 0.01—1.0$;
$H_2O : (M)_{2/n}O = 10—500$; $ROH : Al_2O_3 = 5—500$;
$ROH:NH_3 > 2$. (n is valency of M).

The mixture is maintained at elevated temperature.

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SPECIFICATION

A process for the preparation of zeolites

The invention relates to a process for the preparation of crystalline aluminosilicate zeolites with an SiO_2/Al_2O_3 molar ratio of at least 12 and a constraint index between 1 and 12. Zeolites of this class have been found very suitable to be used as catalysts in many kinds of conversion processes, in particular in the conversion of aliphatic compounds into aromatic hydrocarbons. With a view to the catalytic behaviour, in the greater part of these processes preference is given to zeolites of this class having a crystallite size of less than three microns. Zeolites of this class may be prepared starting from an aqueous mixture containing the following compounds in a given ratio: one or more aluminium compounds, one or more silicon compounds, one or more alkali and/or alkaline-earth metal compounds and one or more quaternary alkylammonium compounds. The preparation is effected by maintaining the mixture at elevated temperature until the zeolite has been formed and then separating the crystals of the zeolite from the mother liquor. Although in this way zeolites are obtained with a crystallite size of less than three microns, which, in addition, are not or practically not contaminated with amorphous material, this method of preparation still has a serious drawback, which is connected with the use of the quaternary alkylammonium compound and which drawback is an obstacle to the use on a technical scale. Quaternary alkylammonium compounds are relatively expensive compounds, which, in view of the amounts required in this method of preparation, are hardly suitable for use in the catalyst preparation on a technical scale.

The Applicant has carried out an investigation concerning possible methods of preparation of the above-mentioned zeolites which do not use the expensive quaternary alkylammonium compounds. In the investigation a certain method of preparation was considered acceptable only if it produced zeolites which were not or hardly not contaminated with amorphous material and if these zeolites had, in addition, a crystallite size of less than three microns. Attempts to replace in the preparation of the zeolites the quaternary alkylammonium compound by an alkylamine, an alcohol or ammonia, have not produced the desired result. In respect of the use of an alkylamine, for instance butylamine, it may be noted that this leads to zeolites with a crystallite size of more than 3 microns. Although the price of alkylamines is, as a rule, lower than that of quaternary alkylammonium compounds, it is still on such a level that it makes the use of these compounds in catalyst preparation on a technical scale doubtful. In respect of the use of an alcohol, for instance n-butanol, it has been found that it leads to zeolites which are highly contaminated with amorphous material. When the quaternary alkylammonium compound is replaced by ammonia, the product obtained is exclusively amorphous material.

A method of preparing zeolites that is satisfactory in every respect has been found to be obtained if the quaternary alkylammonium compound is replaced by a mixture of one or more alcohols and ammonia, whose alcohol/ammonia molar ratio is greater than 2. The preparation of the zeolites is then started from an aqueous mixture in which the various components are present in the following molar ratios, expressed—with the exception of the alcohols and ammonia—in moles of the oxides:

SiO_2	:	Al_2O_3	$\geqslant$	12,
$(M)_{2/n}O$	:	SiO_2	=	0.01—1.0,
H_2O	:	$(M)_{2/n}O$	=	10—50,
ROH	:	Al_2O_3	=	5—500, and
ROH	:	$NH_3 > 2$,		

where M represents one or more alkali and/or alkaline-earth metals, n the valency thereof and where ROH represents one or more alcohols.

The above-mentioned process for the preparation of zeolites satisfies in every respect the requirements made. The expensive quaternary alkylammonium compound has been replaced by a mixture of inexpensive chemicals (alcohols and ammonia); the process produces the zeolites in a very pure form, not or practically not contaminated with amouphous material; the zeolites are obtained in a crystallite size of less than three microns. In comparison with a method of preparing the zeolites using a quaternary alkylammonium compound or, possibly, an alkylamine, the preparation method using a mixture of an alcohol and ammonia has an additional advantage, which is connected with the environment. The use of organic nitrogen compounds, such as quaternary alkylammonium compounds and alkylamines, in processes on a technical scale has great disadvantages in view of contamination of the environment by waste products. The use of a mixture of an alcohol and ammonia does not have this disadvantage.

The finding that an everyway satisfactory synthesis of the zeolites can be effected by using a mixture of one of more alcohols and ammonia with an alcohol/ammonia molar ratio which is greater than 2, is surprising inter alia because it has been found that the use of mixtures of one or more alcohols and ammonia with an alcohol/ammonia molar ratio smaller than 2 gives rise to the formation of a product in which the zeolites occur highly contaminated with amorphous material.

The present patent application therefore relates to a process for the preparation of crystalline aluminosilicate zeolites having an SiO_2/Al_2O_3 molar ratio of at least 12 and a constraint index between 1 and 12, in which process an aqueous mixture containing the following compounds: one or more compounds of an alkali and/or alkaline-earth metal (M), one or more Al compounds, one or more Si compounds, one or more alcohols (ROH) and ammonia, in which mixture the various compounds, are present in the following molar

ratios, expressed—with the exception of the alcohols and ammonia—in moles of the oxides:

SiO_2	:	Al_2O_3	⩾	12,
$(M)_{2/n}O$	:	SiO_2	=	0.01—1.0,
H_2O	:	$(M)_{2/n}O$	=	10—500,
ROH	:	Al_2O_3	=	5—500, and
ROH	:	NH_3>2,		

(n is the valency of M) is maintained at elevated temperature until the zeolite has been formed and in which, subsequently, the crystals of the zeolite are separated from the mother liquor.

Zeolites prepared according to the invention are characterized in that they have a constraint index between 1 and 12. The constraint index of zeolites can be determined in a simple way by continuously passing a mixture of equal quantities by weight of n-haxane and 3-methylpentane at atmospheric pressure over a small sample—about 1 g or less—of the zeolite concerned according to the process given below. A sample of the zeolite, in the form of granules or extrudates, is ground to a particle size which is about equal to that of coarse sand and introduced into a glass tube. Previous to the investigation the zeolite is treated with a stream of air of about 538°C for at least 15 minutes. The zeolite is then purged with helium and the temperature is set to a value between about 285 and 510°C to give a total conversion between 10 and 60%. The mixture of hydrocarbons is passed over the zeolite at a volumetric flow rate of 1 (i.e. 1 volume liquid hydrocarbon per volume zeolite per hour), diluted with helium to such an extent that the molar ratio of helium to total hydrocarbons is 4:1. After a running time of 20 minutes a sample of the effluent is taken and analysed (which can be done best by gas chromatography) in order to determine the fraction of each of the two hydrocarbons which has remained unchanged. The constraint index is calculated as follows

$$\text{Constraint index} = \frac{{}^{10}\log\,(\text{remaining fraction of n-hexane})}{{}^{10}\log\,(\text{remaining fraction of 3-methylpentane})}$$

The constraint index approaches the ratio of the rate constants for cracking the two hydrocarbons.

The process according to the invention is preferably used for the preparation of zeolites which are designated ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38. US patent No. 3,702,886 describes ZSM-5. ZSM-11 is described in US patent No. 3,709,979 and ZSM-12 in US patent No. 3,832,449. US patent applications No. 528,061 and No. 528,060 describe ZSM-35 and ZSM-38, respectively. Particular preference is given to the use of the process according to the invention for the preparation of zeolite ZSM-5.

The zeolite preparation according to the invention may be carried out at atmospheric or at elevated pressure. If reaction temperatures are used which are higher than the boiling point of the mixture, it is preferred to work in an autoclave under autogenous pressure. The zeolites are preferably prepared by maintaining the mixture for at least four hours at a temperature between 90 and 250°C and in particular at a temperature between 125 and 175°C. After the zeolites have been formed, the crystals are separated from the mother liquor, for instance by means of filtering, decanting or centrifuging. The crystal mass is then washed with water and finally dried at a temperature of from 100 to 200°C.

Examples of suitable compounds which may be used in the zeolite preparation according to the invention are: nitrates, carbonates, hydroxides and oxides of alkali and alkaline-earth metals, primary, secondary and tertiary aliphatic alcohols, aluminium hydroxide, sodium aluminate, aluminium sulphate and activated aluminas such as: gamma alumina, sodium silicate, silica gels silicic acid, aqueous colloidal silica sols and amorphous solid silicas such as precipitated silica sols. In the zeolite preparation according to the invention it is preferred to start from a base mixture in which M is present in an alkali metal compound and in which the alcohol is an unbranched primary alcohol and in particular from a base mixture in which M is present in a sodium compound and in which the alcohol is n-butanol.

As regards the molar ratios in which the various compounds are present in the base mixture, preference is given to base mixtures in which:

a)	$(M)_{2/n}O$	:	SiO_2	=	0.05—0.5,
b)	H_2O	:	$(M)_{2/n}O$	=	25—250,
c)	ROH	:	Al_2O_3	=	10—100, and
d)	ROH	:	NH_3	=	2—30.

In the zeolite preparation according to the invention it is highly preferred to start from a base mixture in which the molar ROH:NH_3 ratio lies between 2 and 10.

If the zeolites prepared according to the invention contain alkali metals, and these zeolites are envisaged to be used as catalysts, it is preferable first to reduce the alkali metal content of the zeolites to less than 1%w and in particular to less than 0.05%w. Reduction of the alkali metal content of the zeolites can very conveniently be effected by contacting these once or several times with a solution containing exchangeable cations. For instance, by treating the silicates with a solution containing ammonium ions, NH_4^+-zeolites can be prepared in this way. The H^+-zeolites can be obtained by calcining the NH_4^+-zeolites.

Zeolites prepared according to the invention have catalytic activity and may therefore be used as catalysts without further modification. They may also be used as the catalyst carrier for one or more catalytically active metal components. Metals which can be deposited on the zeolites prepared according to the invention, are—depending on the envisaged use of the catalyst—the metals of Groups IB, IIB, VB, VIB, VIIB and VIII of the Periodic Table. Among these metals are copper, silver, zinc, cadmium,

vanadium, chromium, molybdenum, tungsten, manganese, the metals of the iron group and the metals of the platimum group. The deposition of the metals on the zeolites may be effected in the usual way by impregnation, percolation, ion exchange, and the like. To increase the activity, selectivity and/or stability of the catalysts, promoters such as halogen, magnesiumA phosphorus, boron, arsenic and antimony, may be incorporated into them. Very suitable catalysts for many kinds of processes are catalysts containing one of the following catalytically active metals or metal combinations on a zeolite prepared according to the invention as the carrier: nickel, copper, zinc, cadmium, chromium, platinum, palladium, nickel-tungsten, cobalt-molybdenum, nickel-molybdenum, zinc-palladium, zinc-copper and zinc-rhenium.

When zeolites prepared according to the invention are used for catalytic purposes, the material should generally be available in the form of particles with a diameter of 0.5—5 mm. In the method of preparation according to the invention the zeolites are obtained in the form of a fine powder. The zeolites may be moulded into particles of a larger size, for instance by pressure moulding. In the moulding process the zeolite may, if desired, be combined with an inorganic matrix or binder material. Examples of suitable matrix or binder materials are natural clays such as kaolin and bentonite. Other suitable matrix or binder materials are synthetic inorganic oxides such as alumina, silica, zirconia and the like or combinations thereof, such as silica-alumina and silica-zirconia. When the zeolites prepared according to the invention are combined with a matrix or binder material, any mixing ratio may in principle be used. It is preferred to use a matrix or binder material which does not contain any alkali metal or whose alkali metal content is very low. Catalysts consisting at least partly of a zeolite prepared according to the invention, willm for the sake of brevity, in this patent application further be referred to as "catalysts according to the invention".

Although catalysts according to the invention have very long lives, it is nevertheless desirable to apply a regeneration from time to time. This can simply be done by subjecting the catalyst to a burn-off.

Catalysts according to the invention may, inter alia, be used in the following processes:

1. Catalytic cracking of heavy hydrocarbon oils for the preparation of light hydrocarbon oil distillates;
2. Preparation of isoparaffins by isomerisation of n-paraffins;
3. Hydrodesulphurization of hydrocarbon oil distillates;
4. Conversion of naphthenes into aromatics;
5. Polymerization of olefins for the preparation of polyolefins;
6 Hydrocracking of heavy hydrocarbon oils for the preparation of light hydrocarbon oil distillates;
7. Hydrocracking of heavy hydrocarbon oils for the preparation of lubricating oils with a high viscosity index;
8. Improvement of the light and oxidation stability of lubricating oils which have been prepared in the conventional way or by hydrocracking;
9. Improvement of the quality of gasoline by hydrocracking the n-paraffins present therein;
10. Preparation of olefins from alcohols and/or ethers with not more than four carbon atoms per alkyl group;
11. Hydrodewaxing of lubricating oils;
12. Alkylation of aromatics;
13. Transalkylation of alkyl aromatics;
14. Alkylation of olefins.

The catalysts according to the invention can very suitably be used in the following processes:

1. Catalytic gasoil dewaxing for cloud point improvement;
2. Preparation of p-xylene by isomerization of other C_8 aromatics;
3. Preparation of p-xylene by methylation of toluene;
4. Preparation of p-xylene by disproportionation of toluene.

Although catalysts according to the invention can be successfully used in any of the above-mentioned processes, the great importance of these catalysts lies in another area. For it has been found that these catalysts are pre-eminently suitable for the preparation of aromatic hydrocarbons from aliphatic hydrocarbons and/or oxygen-containing aliphatic hydrocarbons. The aromatization process according to the invention is suitable, in particular, to be applied to a product obtained in the conversion of a H_2/CO mixture over a catalyst containing one or more metal components having catalytic activity for the conversion of H_2/CO mixture into aliphatic hydrocarbons and/or oxygen-containing aliphatic hydrocarbons. The preparation of an aromatic hydrocarbon mixture from a H_2/CO mixture is preferably carried out in one step by contacting the mixture with a bifunctional catalyst containing a zeolite prepared according to the invention and one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into aliphatic hydrocarbons and/or oxygen-containing aliphatic hydrocarbons. The important application of the zeolites prepared according to the invention is in the field of the preparation of an aromatic hydrocarbon mixture from coal, by gasification of the coal at a temperature higher than 1000°C into a H_2/CO mixture and conversion of this mixture in one step into an aromatic hydrocarbon mixture by contacting it with a trifunctional catalyst containing a zeolite prepared according to the invention, one or more metal components having catalytic activity for the conversion of a H_2/CO mixture into aliphatic hydrocarbons and/or oxygen-containing aliphatic hydrocarbons and one or more metal components having catalytic activity for the water gas shift reaction.

Very suitable catalyst components having catalytic activity for the conversion of a H_2CO

mixture into aliphatic hydrocarbons and/or oxygen-containing aliphatic hydrocarbons are the metals iron and cobalt and the metal combination zinc-chromium.

The aromatization process according to the invention is also very suitable for the preparation of p-xylene from lower aliphatic hydrocarbons such as propene or from lower oxygen-containing aliphatic hydrocarbons such as methanol.

In addition to their use as catalyst or catalyst carrier the zeolites prepared according to the invention are also suitable to be used for many other purposes, such as adsorbent, extracting agent, drying agent, ion exchanger and molecular sieve. Of these other applications, it is especially the use as an adsorbent for the separation of p-xylene from mixtures of xylenes that is considered to be important.

The invention is now further explained with reference to the following examples.

EXAMPLE I

Zeolite ZSM-5 wat prepared as follows:

A mixture of SiO_2, $NaAlO_2$, NaOH and $[(C_3H_7)_4N]OH$ in water with the molar composition $3.0\ Na_2O.Al_2O_3.\ 13.5[(C_3H_7)_4N]_2O.\ 75\ SiO_2.\ 1350\ H_2O$ was heated in an autoclave at 150°C under autogenous pressure for 24 hours. After the reaction mixture has cooled down, the zeolite formed was filtered off, washed with water until the pH of the wash water was about 8 and dried at 120°C for two hours. In this way pure zeolite ZSM-5 was obtained with a crystallite size of less than 1 micron.

EXAMPLE II

Zeolite ZSM-5 was prepared as follows:

An initial mixture of $n\text{-}C_4H_9NH_2$, water glass (28%w SiO_2; 8%w Na_2O) and water was mixed with a second mixture of $Al_2(SO_4)_3$, H_2SO_4 and water. The mixture thus obtained, which had the following molar composition: $27.0\ Na_2O.Al_2O_3.\ 36.7\ C_4H_9NH_2.\ 93.5\ SiO_2.\ 970\ H_2O$ and in which the H_2SO_4/SiO_2 molar ratio was 0.2, was stirred at room temperature for two hours and then heated in an autoclave under autogenous pressure for 24 hours with stirring. After cooling, the zeolite formed was filtered off, washed with water until the pH of the wash water was about 8 and dried at 120°C for two hours. In this way pure zeolite ZSM-5 was obtained with a crystallite size of more than 3 microns.

EXAMPLE III

Zeolite ZSM-5 was prepared in substantially the same way as described in Example II, the differences being, however, that the initial mixture now contained $n\text{-}C_4H_9OH$ instead of $n\text{-}C_4H_9NH_2$ and that the ultimate mixture had the following molar composition: $25.9\ Na_2O.\ Al_2O_3.\ 34.8\ C_4H_9OH.\ 88.4\ SiO_2.\ 1820\ H_2O$. In this way zeolite ZSM-5 was obtained, which was contaminated with about 20%w amorphous material.

EXAMPLE IV

Zeolite ZSM-5 was prepared in substantially the same way as described in Example III, the differences being, however, that the second mixture now contained, in addition, NH_3, and that the ultimate mixture has the following molar composition $25.9\ Na_2O.Al_2O_3.\ 15\ C_4H_9OH.\ 55\ NH_3.\ 88.4\ SiO_2.\ 1820\ H_2O$. In this way zeolite ZSM-5 was obtained, which was contaminated with about 10%w amorphous material.

EXAMPLE V

Zeolite ZSM-5 was prepared in substantially the same way as described in Example IV, the difference being, however, that the ultimate mixture now had the following molar composition $25.9\ Na_2O.\ Al_2O_3.\ 55\ C_4H_9OH.\ 15\ NH_3.\ 88.4\ SiO_2.\ 1820\ H_2O$. In this way very pure ZSM-5 was obtained with a crystallite size of less than 2 microns.

CLAIMS

1. A process for the preparation of crystalline aluminosilicate zeolites having an SiO_2/Al_2O_3 molar ratio of at least 12 and a constraint index between 1 and 12, characterised in that an aqueous mixture containing the following compounds:

one or more compounds of an alkali and/or alkaline-earch metal (M), one or more Al-compounds, one or more Si-compounds, one or more alcohols (ROH) and ammonia, in which mixture the various compounds are present in the following molar ratios, expressed—with the exception of the alcohols and ammonia—in moles of the oxides:

SiO_2	:	Al_2O_3	$\geqslant$	12,
$(M)_{2/n}O$	:	SiO_2	=	0.01—1.0,
H_2O	:	$(M)_{2/n}O$	=	10—500,
ROH	:	Al_2O_3	=	5—500, and
ROH	:	$NH_3>2$,		

(n is the valency of M) is maintained at elevated temperature until the zeolite has been formed and in that subsequently the crystals of the zeolite are separated from the mother liquor.

2. A process according to claim 1, characterized in that the aqueous mixture is maintained, for at least four hours, at a temperature between 90 and 250°C.

3. A process according to claim 1 or 2, characterized in that in the aqueous mixture M is present in an alkali metal compound.

4. A process according to any one of claims 1—3, characterized in that the aqueous mixture ROH is present as an unbranched primary alcohol.

5. A process according to any one of claims 1—4, characterized in that the various compounds are present in the aqueous mixture in the following molar ratios:

a)	$(M)_{2/n}O$	:	SiO_2	=	0.05—0.5,
b)	H_2O	:	$(M)_{2/n}O$	=	25—250,
c)	ROH	:	Al_2O_3	=	10—100, and
d)	ROH	:	NH_3	=	2:30.

6. A process according to claim 5, characterized in that the molar ROH/NH_3 ratio in the aqueous mixture lies between 2 and 10.

7. A process for the preparation of crystalline aluminosilicate zeolites with an SiO_2/Al_2O_3 molar ratio of at least 12 and a constraint index between 1 and 12, as claimed in claim 1 as described hereinbefore with reference to Example V.

8. Crystalline aluminosilicate zeolites with an SiO_2/Al_2O_3 molar ratio of at least 12 and a constraint index between 1 and 12, prepared according to a process as described in any one of the preceding claims.

9. Catalysts, characterized in that they contain a zeolite according to claim 8 loaded with one or more metal components from Groups IB, IIB, VB, VIB, VIIB and/or VIII of the Periodic Table.

10. A process for carrying out a catalytic conversion characterized in that use is made of a catalyst according to claim 10 or 11.

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